

⑫

EUROPEAN PATENT APPLICATION

⑳ Application number: 89100260.2

⑪ Int. Cl.⁴: **C08G 59/06 , C08G 59/14 ,
C08G 59/50**

㉔ Date of filing: 09.01.89

㉓ Priority: 13.01.88 US 143771

㉒ Date of publication of application:
19.07.89 Bulletin 89/29

㉑ Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE

㉑ Applicant: **THE DOW CHEMICAL COMPANY**
Office of Patent Counsel P.O. Box 1967
Midland Michigan 48640(US)

㉒ Inventor: **Massingill, John L., Jr.**
410 Forest Drive
Lake Jackson Texas 77566(US)
Inventor: **Pabon, Raul A., Jr.**
106 Mesquite
Lake Jackson Texas 77566(US)

㉒ Representative: **Sternagel, Hans-Günther, Dr.**
et al
Patentanwälte Dr. Michael Hann Dr. H.-G.
Sternagel Sander Aue 30
D-5060 Bergisch Gladbach 2(DE)

㉒ **Modified advanced epoxy resins.**

㉒ Modified advanced epoxy resins are prepared by reacting (A) an advanced epoxy resin prepared by reacting (1) an epoxy resin having at least one aromatic ring, an average of more than one, but not more than about 2 vicinal epoxy groups per molecule and which contains at least one oxyalkylene or substituted oxyalkylene group per molecule; with (2) a dihydric phenol; with (B) a monoamine. Curable compositions comprising the modified advanced epoxy resin and cured products resulting from curing the curable compositions are also disclosed.

EP 0 324 405 A2

MODIFIED ADVANCED EPOXY RESINS

The present invention concerns advanced epoxy resins prepared from dihydric phenols and compounds having an average of more than one glycidyl ether group per molecule, at least one aromatic group per molecule and at least two alkoxy groups per molecule which advanced epoxy resins have been reacted with an amine.

- 5 Advanced aromatic epoxy resins are well known for their extremely useful combination of properties such as flexibility, adhesion, resistance to corrosion, and chemical and solvent resistance. Unfortunately, they also have some well known disadvantages such as sensitivity to ultraviolet light, relatively high viscosities, and limited formability. Advanced aliphatic epoxy resins are well known for their low viscosities and flexibility; however, they lack physical strength and are sensitive to water and chemicals. It would be
10 desirable to have available advanced epoxy resins which have unique combinations of viscosity (low), and when cured with a suitable curing agent, good flexibility, strength and resistance to water and chemicals and solvents.

One aspect of the present invention pertains to a modified advanced epoxy resin which results from reacting

- 15 (A) an advanced epoxy resin which results from reacting
(1) an epoxy resin composition comprising
(a) at least one epoxy resin having at least one aromatic ring, an average of more than one, but not more than two vicinal epoxy groups per molecule and which contains at least one oxyalkylene or substituted oxyalkylene group per molecule; and
20 (b) optionally at least one epoxy resin which has an average of more than one but not more than two vicinal epoxy groups per molecule and which is different from the epoxy resin of (a) above;
wherein components (a) and (b) are present in amounts such that from 5 to 100 equivalent percent of the epoxide groups are derived from component (a) and from zero to 95 equivalent percent of the epoxide groups are derived from component (b); with
25 (2) at least one compound having two aromatic hydroxyl groups per molecule;
wherein components (1) and (2) are employed in amounts which provide a ratio of aromatic hydroxyl groups per epoxy group of from 0.005:1 to 200:1; with
(B) a nitrogen-containing compound selected from (1) primary monoamines;
(2) secondary monoamines;
30 (3) tertiary monoamines;
(4) hydroxyl substituted primary, secondary or tertiary monoamines; or
(5) any combination of components (B-1), (B-2), (B-3) or (B-4);
wherein components (A) and (B) are present in an amount such that the ratio of amine groups contained in component (B) to epoxy groups contained in component (A) is from 0.1:1 to 1.1:1.

- 35 Another aspect of the present invention pertains to a curable composition which comprises (I) the aforesaid reaction product of the advanced epoxy resin and nitrogen-containing compound and (II) a curing amount of a suitable curing agent for component (I).

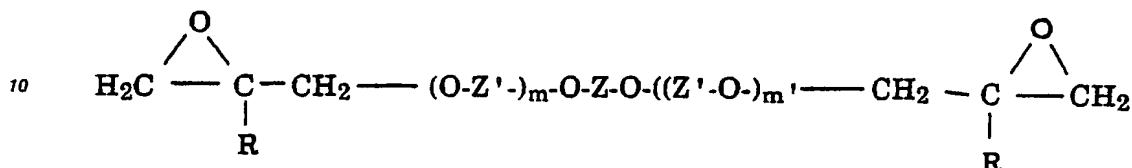
- 40 The compositions of the present invention have unique combinations of viscosity (low), and when cured with a suitable curing agent, good flexibility, strength and resistance to water and chemicals and solvents.

- The advanced epoxy resins employed in the present invention are prepared by reacting the epoxy resin or mixture of epoxy resins with the compound having two aromatic hydroxyl groups per molecule or mixture of such compounds at a temperature suitably from 25°C to 300°C, more suitably from 50°C to 250°C, most suitably from 50°C to 225°C for a time sufficient to complete the reaction, suitably from 1 to 8, more
45 suitably from 1 to 6, most suitably from 1 to 4 hours. The higher the temperature, the shorter the reaction time and the lower the temperature the longer the reaction time. The reaction is usually conducted in the presence of a catalyst and if desired, one or more solvents. The reactants are employed in amounts such that the ratio of phenolic hydroxyl groups to epoxide group is suitably from 0.005:1 to 200:1, more suitably from 0.5:1 to 5:1, most suitably from 0.5:1 to 1:1.

- 50 The epoxy resin which is advanced with the compound having two aromatic hydroxyl groups has suitably from 5 to 100, more suitably from 10 to 100, most suitably from 25 to 100 percent of the epoxy groups derived from an epoxy resin which contains oxyalkylene or substituted oxyalkylene groups and suitably from zero to 95, more suitably from zero to 90, most suitably from 5 to 75 percent of the epoxy groups derived from an epoxy resin which is different from the aforementioned epoxy resin.

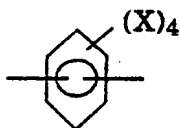
Suitable epoxy resins having at least one aromatic ring, an average of more than one, but not more than about two glycidyl ether groups per molecule and which contain at least one oxyalkylene or substituted oxyalkylene group per molecule include those represented by the following formula I

Formula I

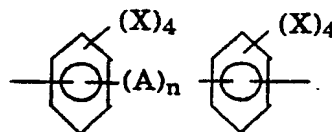


wherein each R is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms, preferably hydrogen or methyl, most preferably hydrogen; Z is a divalent aromatic group represented by the following formulas II and III

Formula II

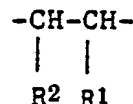


Formula III



wherein A is a divalent hydrocarbyl group having suitably from 1 to 12, more suitably from 1 to 6, most suitably from 1 to 3, carbon atoms, -S-, -S-S-, -SO-, -SO₂-, -CO-, or -O-; each X is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having suitably from 1 to 12, more suitably from 1 to 6, most suitably from 1 to 3 carbon atoms, or a halogen, more suitably chlorine or bromine, most suitably bromine; n is zero or 1; each Z' is independently a group represented by the following formula IV

Formula IV



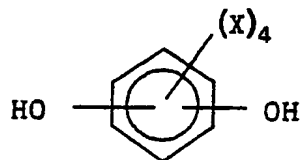
wherein each R¹ and R² are independently hydrogen or a hydrocarbyl or hydrocarbyloxy group having suitably from 1 to 12, more suitably from 1 to 6, most suitably from 1 to 3 carbon atoms or an -CH₂-O-R³ group wherein R³ is a hydrocarbyl group having suitably from 1 to 12, more suitably from 1 to 9, most suitably from 1 to 6 carbon atoms; and each m and m' independently has a value suitably from 1 to 25, more suitably from 1 to 10, most suitably from 1 to 5.

The term hydrocarbyl as employed herein means any aliphatic, cycloaliphatic, aromatic, aryl substituted aliphatic or cycloaliphatic, or aliphatic or cycloaliphatic substituted aromatic groups. The aliphatic groups can be saturated or unsaturated. Likewise, the term hydrocarbyloxy means a hydrocarbyl group having an oxygen linkage between it and the object to which it is attached.

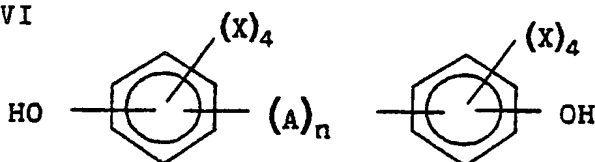
Particularly suitable epoxy resins which have an average of more than one but not more than two vicinal epoxy groups and at least one aromatic ring per molecule and at least one oxyalkylene group or substituted oxyalkylene group per molecule include, for example, the glycidyl ethers of the reaction products of (1) an aromatic compound having two aromatic hydroxyl groups per molecule or mixture of such compounds and (2) an alkylene or substituted alkylene oxide or monoglycidyl ether or any combination thereof.

Suitable compounds having two aromatic hydroxyl groups per molecule which can be employed herein include, for example, those represented by the following formulas V and VI

Formula V



Formula VI

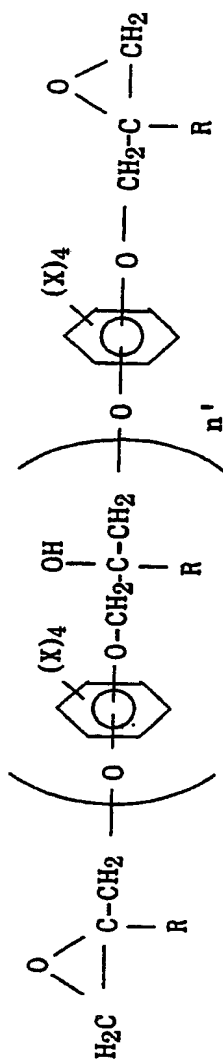


wherein A, X and n are as defined above.

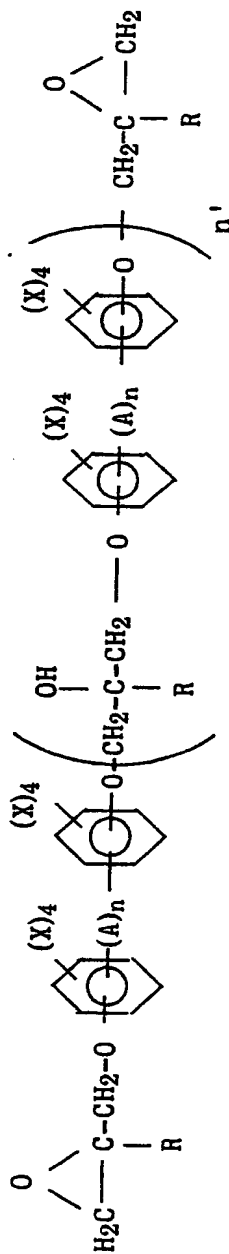
Particularly suitable aromatic compounds having two aromatic hydroxyl groups per molecule include, for example, catechol, hydroquinone, resorcinol, biphenol, bisphenol A, bisphenol F, bisphenol K, bisphenol S, and combinations thereof. Particularly suitable alkylene oxides include, for example, ethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide and combinations thereof. Particularly suitable substituted alkylene oxides include, for example, styrene oxide, t-butyl styrene oxide, isopropenyl benzene oxide and combinations thereof. Suitable monoglycidyl ethers include, for example, glycidyl ethers of ethylenically unsaturated monocarboxylic acids, alkyl glycidyl ethers, aryl glycidyl ethers and combinations thereof. Particularly suitable monoglycidyl ethers include, for example, phenyl glycidyl ether, butyl glycidyl ether, glycidyl acrylate, glycidyl methacrylate, dodecyl glycidyl ether and combinations thereof.

Suitable epoxy resins which have an average of more than one but not more than two vicinal epoxy groups per molecule and which are different from the aforementioned epoxy resins include, for example, those aromatic epoxy resins represented by the following formulas VII and VIII as well as those aliphatic epoxy resins represented by the following formula IX

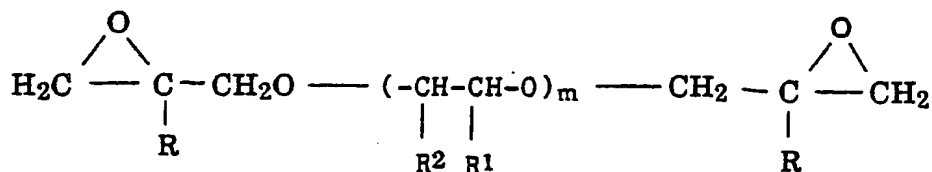
Formula VII



Formula VIII



Formula IX

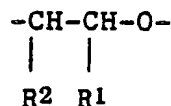


wherein A, R, R¹, R², X, m and n are as defined above and n' suitably has an average value from zero to 5, more suitably from 0.01 to 0.5, most suitably from 0.03 to 0.15.

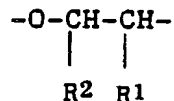
Particularly suitable as the other epoxy resins are those epoxy resins which have an average of more than one but not more than two vicinal epoxy groups and at least one aromatic ring per molecule which are free of oxyalkylene or substituted oxyalkylene groups.

The term free of oxyalkylene or substituted oxyalkylene groups means that the epoxy resin is free of groups represented by the following formulas X and XI

Formula X



Formula XI



wherein R¹ and R² are as defined above.

More particularly suitable epoxy resins which have an average of more than one but not more than two vicinal epoxy groups and at least one aromatic ring per molecule and which are free of oxyalkylene groups include, for example, the glycidyl ethers of catechol, resorcinol, hydroquinone, biphenol, bisphenol A, bisphenol F, bisphenol K, bisphenol S, and any combination thereof.

The epoxy resins which are prepared from compounds having aliphatic hydroxyl groups which are reacted with an epihalohydrin can be prepared by any of the known methods for preparing aliphatic epoxy resins such as conducting the reaction in the presence of a Lewis acid such as, for example, stannic chloride, boron trifluoride and combinations thereof; followed by dehydrohalogenation with a basic acting compound such as an alkali metal hydroxide. Most preferably, these epoxy resins are prepared by the method disclosed in GB 2,137,205A.

Suitable catalysts which can be employed to prepare the advanced epoxy resins include, for example, tertiary amines, phosphines, ammonium compounds, phosphonium compounds and metal hydroxide. Particularly suitable catalysts include, ethyl triphenyl phosphonium chloride, ethyl triphenyl phosphonium bromide, ethyl triphenyl phosphonium iodide, ethyl triphenyl phosphonium acetate-acetic acid complex, tetrabutyl phosphonium chloride, tetrabutyl phosphonium bromide, tetrabutyl phosphonium iodide, tetrabutyl phosphonium acetate-acetic acid complex and combinations thereof. The catalyst is suitably employed in an amount which corresponds to from 0.0001 to 0.02, more suitably from 0.002 to 0.02, most suitably from 0.002 to 0.02, moles of catalyst per mole of epoxy resin.

Suitable solvents which can be employed in the preparation of the advanced epoxy resins include, for example, alcohols, ketones, glycol ethers, aliphatic hydrocarbons, halogenated aliphatic hydrocarbons, aromatic hydrocarbons and combinations thereof. Particularly suitable solvents include, for example, toluene, xylene, propylene glycol methyl ether, propylene glycol butyl ether, propylene glycol monotertiary butyl ether, ethylene glycol monobutyl ether (2-butoxyethanol) and combinations thereof. The solvent can be employed suitably in amounts of from zero to 50, more suitably from 3 to 30, most suitably from 3 to 20 percent by weight based upon combined weight of the epoxy resin and the phenolic compound.

Suitable nitrogen-containing compounds which can be employed herein to react with the advanced epoxy resins include, for example, ammonia, primary monoamines, secondary monoamines and tertiary

monoamines. Suitable primary monoamines include those aliphatic and aromatic primary monoamines having suitably from zero to 20, more suitably from 2 to 10, most suitably from 2 to 7, carbon atoms. Suitable such primary monoamines include, for example, ammonia, ethyl amine, ethanol amine and combinations thereof. Suitable secondary monoamines include those aliphatic and aromatic secondary
 5 monoamines having suitably from 2 to 20, more suitably from 2 to 10, most suitably from 2 to 7, carbon atoms. Suitable such secondary monoamines include, for example, diethylamine, diethanolamine, methyl ethanolamine and combinations thereof. Suitable tertiary monoamines include those aliphatic and aromatic tertiary monoamines having suitably from 3 to 20, more suitably from 3 to 10, most suitably from 3 to 6
 10 carbon atoms. Suitable such tertiary monoamines include, for example, methyl diethanolamine and combinations thereof.

Particularly suitable nitrogen-containing compounds which can be employed to modify the advanced epoxy resins to prepare the modified advanced epoxy resins of the present invention include the hydroxyl-containing monoamines such as, for example, dimethyl ethanolamine, methyl dimethanolamine, ethanolamine, methyl ethanolamine and combinations thereof.

15 The nitrogen-containing compound is employed in an amount which provides a ratio of amine groups contained in the nitrogen-containing compound, component (B), to epoxy groups contained in the advanced epoxy resin, component (A), suitably from 0.1:1 to 1.1:1, more suitably from 0.1:1 to 1:1, most suitably from 0.15:1 to 1:1.

If desired, the modified advanced epoxy resins of the present invention can be further modified with a
 20 volatile acid to prepare a quaternary ammonium compound. Suitable such acids include, for example, any aliphatic monocarboxylic acid having suitably from 1 to 10, more suitably from 2 to 4, most suitably from 2 to 3 carbon atoms. Particularly suitable aliphatic monocarboxylic acids include, for example, acetic acid, propionic acid lactic acid and combinations thereof. The acid can be employed in amounts which provides a ratio of acid equivalents per amine group suitably from 0.8:1 to 1.3:1, more suitably from 0.9:1 to 1.1:1,
 25 most suitably from 0.95:1 to 1:1.

The modified advanced epoxy resins of the present invention can be cured with any suitable curing agent for epoxy resins including, for example, primary and secondary polyamines, carboxylic acids and anhydrides thereof, phenolic hydroxyl-containing compounds, guanidines, biguanides, urea-aldehyde resins, melamine-aldehyde resins, alkoxyated urea-aldehyde resins, alkoxyated melamine-aldehyde resins,
 30 phenol-aldehyde (resole) resins and combinations thereof. Particularly suitable curing agents include, for example, diethylenetriamine, Nadic methyl anhydride, phenol-formaldehyde (resole) resins, cresol-formaldehyde (resole) resins, bisphenol A-formaldehyde (resole) resins, melamine-formaldehyde resins, methoxylated melamine-formaldehyde resins, urea-formaldehyde resins, methoxylated urea-formaldehyde resins and combinations thereof. The curing agents are employed in an amount which will effectively cure the
 35 composition containing the epoxy resin. These amounts will depend upon the particular epoxy resin and curing agent employed; however, suitable amounts include, for example, from 0.025 to 4, more suitably from 0.5 to 2, most suitably from 0.75 to 1.25 equivalents of curing agent per epoxide equivalent for those curing agents which cure by reacting with the epoxy group of the epoxy resin or per hydroxyl group for those curing agents which cure by reacting with the aliphatic hydroxyl groups along the backbone of the
 40 epoxy resin.

The advanced epoxy resins of the present invention can be blended with other materials such as solvents or diluents, fillers, pigments, dyes, flow modifiers, thickeners, reinforcing agents, accelerators and combinations thereof.

These additives are added in functionally equivalent amounts e.g., the pigments and/or dyes are added
 45 in quantities which will provide the composition with the desired color; however, they are suitably employed in amounts of from 1 to 200, more suitably from 10 to 100, most suitably from 50 to 100 percent by weight based upon the weight of the resin binder.

Solvents or diluents which can be employed herein include, for example, hydrocarbons, ketones, glycol ethers, chlorinated solvents, esters and combinations thereof. Particularly suitable solvents or diluents
 50 include, for example, toluene, benzene, xylene, methyl ethyl ketone, methyl isobutyl ketone, diethylene glycol methyl ether, dipropylene glycol methyl ether, ethylene glycol butyl ether, propylene glycol methyl ether, 1,1,1-trichloroethane, DuPont DBE dibasic ester, ethylacetate, propylene glycol t-butyl ether and combinations thereof.

Reinforcing materials which can be employed herein include natural and synthetic fibers in the form of
 55 woven mat, monofilament, multifilament, and the like. Suitable reinforcing materials include, glass, ceramics, nylon, rayon, cotton, aramid, graphite and combinations thereof.

Suitable fillers which can be employed herein include, for example, inorganic oxides, ceramic microspheres, plastic microspheres and combinations thereof.

EP 0 324 405 A2

The advanced epoxy resin compositions of the present invention can be employed in the preparation of coatings, castings, laminates, composites, encapsulants, and potting compositions.

5 Example 1

(A) Preparation of Glycidyl Ether of Reaction Product of Bisphenol A and Propylene Oxide.

10 Into a reaction vessel equipped with stirrer, temperature controller, condenser and nitrogen pad containing 500 g of ethylene dichloride was dissolved, at 75 °C, 172 g (1 OH equiv.) of the reaction product of propylene oxide and bisphenol A in a molar ratio of 2 to 1, respectively. Stannic chloride, 5 g (0.02 equiv.) is added and the temperature was raised to reflux, 88 °C. Epichlorohydrin, 194 g (1.2 equiv.) was added over a 45 minute period from a dropping funnel. The solution turned black. The reaction mixture was
15 cooled to 70 °C and 6 ml (0.0166 moles) of a 60 percent aqueous solution of benzyl trimethylammonium chloride and 500 g (2.5 moles) of a 20 percent aqueous solution of sodium hydroxide were added and the reaction mixture cooled to 50 °C. Stirring was continued and the mixture maintained at 50 °C for 2 hours. The reaction mixture was cooled to 35 °C and the aqueous layer was separated from the organic layer. To the organic layer was added an additional 250 g (1.25 moles) of 20 percent aqueous sodium hydroxide and
20 3 ml (0.008 moles) of a 60 percent aqueous solution of benzyl trimethylammonium chloride catalyst was added. The reaction mixture was heated to 50 °C and maintained thereat with stirring for 2 hours. The reaction mixture was cooled to 35 °C and the aqueous layer was separated from the organic layer. The organic layer was washed three times with 150 ml portions of water. The ethylene dichloride was removed under vacuum in a rotary evaporator at 150 °C. The resultant product had an epoxide equivalent weight (EEW) of 301.75, an aliphatic hydroxyl content of 1.86 wt. percent and a viscosity of 4040 cps (4.04 Pa·s) at 25 °C.

(B) Preparation of Advanced Epoxy Resin.

30 A diglycidyl ether of bisphenol A having an EEW of 180, 152.7 g (0.85 epoxy equiv.), was blended with 356.2 g (1.18 epoxy equiv.) of the product from A above. This mixture was heated to 80 °C at which time 191.2 g (1.68 equiv.) of bisphenol A was added. After the bisphenol A has dissolved, 0.727 g of a 70 wt. percent methanolic solution of ethyl triphenyl phosphonium acetate-acetic acid complex catalyst was added. The reaction mixture was heated to 150 °C and the heat source was turned off. The reaction
35 exotherm caused the temperature to rise to 190 °C, which temperature was maintained for 4 hours. The resultant advanced epoxy resin had an EEW of 1991.

40 (C) Modification of Advanced epoxy resin.

To 50 g (0.025 equiv.) of the advanced epoxy resin prepared in (B) above was mixed 12.5 g of ethylene glycol monobutyl ether in a three neck 250 ml round bottom flask equipped with a temperature controller, condenser, and nitrogen pad. The mixture was heated to 115 °C with stirring to dissolve the resin. A mixture
45 of 11.3 g water, 2.24 g (0.025 equiv.) of dimethylethanol amine and 1.51 g (0.025 equiv.) of acetic acid was added to the resin solution at 90 °C to 95 °C over a 5 minute period. Heating and stirring was continued for 4.25 hours. The solution was dispersed by the dropwise addition of 56.8 g of water over a 15 minute period resulting in a dispersion containing 40 percent nonvolatiles by weight. The percent nonvolatiles was reduced to 30 percent by the addition of 45 g of water over a period of 10 minutes. The product was nearly
50 transparent with a bluish tinge. The pH of the product was 6.9, the Ford #4 cup viscosity at 25 °C was 15.6 seconds and the volatile organic content (VOC) is approximately 1.6 lbs/gallon (191.7 kg/m³).

(D) Preparation of Coating.

55 A portion of the modified advanced epoxy resin prepared in C above was mixed with a melamine curing agent (CYMEL™ 325 commercially available from American Cyanamid Company) at levels of 15, 20 and 25 phr (parts per hundred parts by weight of the modified advanced epoxy resin). These formulations were

EP 0 324 405 A2

coated onto cold rolled steel panels using a drawdown bar. The coating was cured by baking in an electric convection oven at 400 °F (204.4 °C) for 10 minutes solid epoxy resin).

SOLVENT RESISTANCE was measured by rubbing the coating with a 2-pound (0.9 Kg) ballpeen hammer where the hammer head was covered with gauze and soaked in methyl ethyl ketone (MEK). The number of double rubs, push-pull motion, observed until a marring of the coating occurs was recorded.

FLEXIBILITY was measured by the wedgebend test according to ASTM D3281-84 and/or the T-bend test according to ASTM D4145-83.

REVERSE IMPACT was determined by the procedure of ASTM D2794.

The properties are given in Table I.

COMPARATIVE EXPERIMENT A

(1) Modification of Advanced Epoxy Resin.

The procedure of Example 1-C was repeated using an aromatic advanced epoxy resin instead of the advanced epoxy resin prepared in Example 1-B. To 200 g (0.103 equiv.) of a diglycidyl ether of bisphenol A advanced with bisphenol A and having an an EEW of 1941 commercially available from The Dow Chemical Company as D.E.R.TM 667 was added 50 g of ethylene glycol monobutyl ether. The mixture was heated to 125 °C with stirring to dissolve the resin. A mixture of 46.4 g water (2.58 equiv.), 6.9 g (0.077 equiv) dimethylethanol amine, and 5.9 g (0.098 equiv.) glacial acetic acid was added to the resin solution at 90 °C to 95 °C over a 15 minute period. The mixture was stirred for 4.5 hours at 90 °C. The solution was dispersed by the dropwise addition of 400 g of deionized water over a 1 hour period resulting in a dispersion of the modified advanced epoxy resin. The product was milky white and opaque. The pH of the product was 6.2, the Ford #4 cup viscosity at 25 °C was 14.4 seconds, and the VOC was 1.6 lbs/gal (0.192 kg/l).

2. Preparation of Coating

The above dispersion was formulated as described in Example 1-D using 15, 20 and 25 phr of CYMELTM 325 as a curing agent. These formulations are coated onto cold rolled steel panels using a drawdown bar. The coating was cured by baking in an electric convection oven at 400 °F (204.4 °C) for 10 minutes. The properties of the coatings prepared from this modified advanced epoxy resin are given in the Table.

COMPARATIVE EXPERIMENT B

The procedure of Example 1-A was repeated using an advanced epoxy resin derived from a blend of aliphatic liquid epoxy resin and aromatic liquid epoxy resin.

(1) Preparation of Advanced Epoxy Resin

A diglycidyl ether of bisphenol A having an EEW of 180, 300 g (1.67 equiv.) was blended with a diglycidyl ether of polypropylene glycol having an EEW of 320, 200 g (0.625 equiv.) and the blend was reacted with bisphenol A, 151 g (1.32 equiv.). The reactants were blended and heated to 80 °C. After the bisphenol A was dissolved, 0.95 g of a 70 wt. percent methanolic solution of ethyl triphenyl phosphonium acetate-acetic acid complex catalyst was added. The reaction mixture was heated to 150 °C and the heat source turned off. The reaction exotherm caused the temperature to rise to 185 °C, which temperature was maintained for 4 hours. The resultant advanced epoxy resin had an EEW of 1886.

(2) Modification of Advanced Epoxy Resin

The advanced epoxy resin prepared above was modified as described in Example 1-C. To 200 g (0.106

EP 0 324 405 A2

equiv.) of the advanced epoxy resin prepared in comparative experiment B-1 above was added 50 g of ethylene glycol monobutyl ether. The mixture was heated to 125° C with stirring to dissolve the resin. A mixture of 47.7 g (2.65 equiv.) water, 7.9 (0.079 equiv.) dimethylethanol amine, and 6 g (0.1 equiv.) glacial acetic acid was added to the resin solution at 90° C to 95° C over a 15 minute period. The mixture was stirred for 4.5 hours at 90° C. The solution was dispersed by the dropwise addition of 400 g deionized water over a 1 hour period resulting in a dispersion of the advanced epoxy resin. The product was creamy white and opaque. The pH of the product was 6.8, the Ford #4 cup viscosity at 25° C was 14.1 seconds, and the VOC was 1.6 lbs/gal. (0.192 kg/l). The resultant dispersion settled out after one week, but it was readily redispersible.

(3) Preparation of Coating

The dispersion prepared in comparative experiment B-2 above was formulated as described in Example 1-D using 15, 20 and 25 phr of CYMEL™ 325 as a curing agent. These formulations were coated onto cold rolled steel panels using a drawdown bar. The coating was cured by baking in an electric convection oven at 400° F (204.4° C) for 10 minutes. The properties of the coatings prepared from this modified advanced epoxy resin are given in the Table.

Ex. or Comp. Expt.	Amount of Curing Agent phr	Flexibility T-Bend ^a	Rev. Impact		MEK Double Rubs
			in-lbs	kg-cm	
1	15	T3	80	92	20
1	20	T3	72	83	35
1	25	T3	72	83	45
A*	15	T3	70	81	15
A*	20	T4	60	69	40
A*	25	T5	40	46	95
B*	15	T4	80	92	12
B*	20	T4	60	69	15
B*	25	T5	50	58	18

*Not an example of the present invention.

^aThe lower the T value, the more flexible the coating.

Claims

1. A modified advanced epoxy resin which results from reacting

(A) an advanced epoxy resin which results from reacting

(1) an epoxy resin composition comprising (a) at least one epoxy resin having an average of more than one, but not more than two vicinal epoxy groups per molecule and which contains at least one oxyalkylene or substituted oxyalkylene group per molecule;

(2) at least one compound having two aromatic hydroxyl groups per molecule;

wherein components (1) and (2) are employed in amounts which provide a ratio of aromatic hydroxyl groups per epoxy group of from 0.005:1 to 200:1; with

(B) a nitrogen-containing compound selected from

(1) primary monoamines;

(2) secondary monoamines;

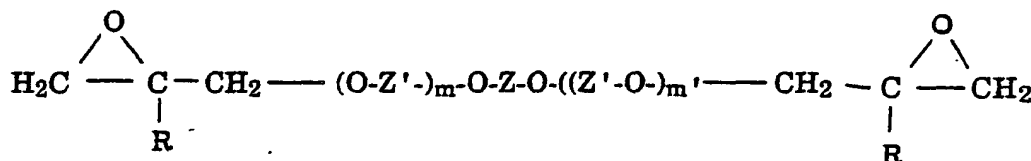
(3) tertiary monoamines;

- (4) hydroxyl substituted primary, secondary or tertiary monoamines; or
 (5) any combination of components (B-1), (B-2), (B-3) or (B-4);
 wherein components (A) and (B) are present in an amount such that the ratio of amine groups contained in component (B) to epoxy groups contained in component (A) is from 0.1:1 to 1.1:1.

2. A modified advanced epoxy resin of Claim 1 wherein component (A-1) further comprises (A-1-b) at least one epoxy resin which has an average of more than one but not more than two vicinal epoxy groups per molecule and which is different from the epoxy resin of (A-1-a);
 wherein components (A-1-a) and (A-1-b) are present in amounts such that from 5 equivalent percent of the epoxide groups are derived from component (A-1-a) and from 5 to 95 equivalent percent of the epoxide groups are derived from component (A-1-b).

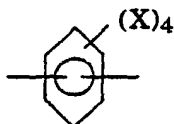
3. An advanced epoxy resin of Claim 2 wherein

(a) component (A-1-a) is an epoxy resin or mixture of epoxy resins represented by the following formula I

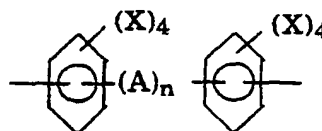


wherein each R is independently hydrogen or an alkyl group having from 1 to 4 carbon atoms; Z is a divalent aromatic group represented by the following formulas II and III

Formula II

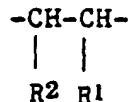


Formula III



wherein A is a divalent hydrocarbyl group having from 1 to 12 carbon atoms, -S-, -S-S-, -SO-, -SO₂-, -CO-, or -O-; each X is independently hydrogen, a hydrocarbyl or hydrocarbyloxy group having from 1 to 12 carbon atoms, or a halogen; n is zero or 1; each Z' is independently a group represented by the following formula IV

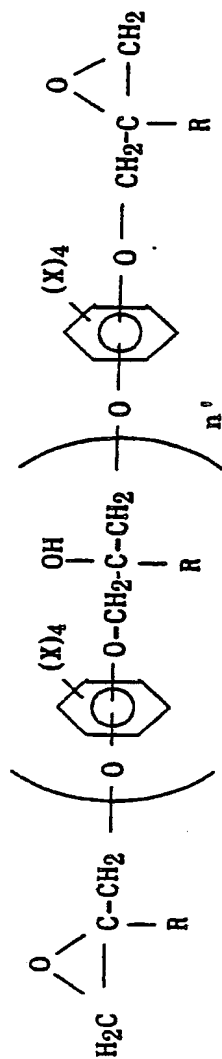
Formula IV



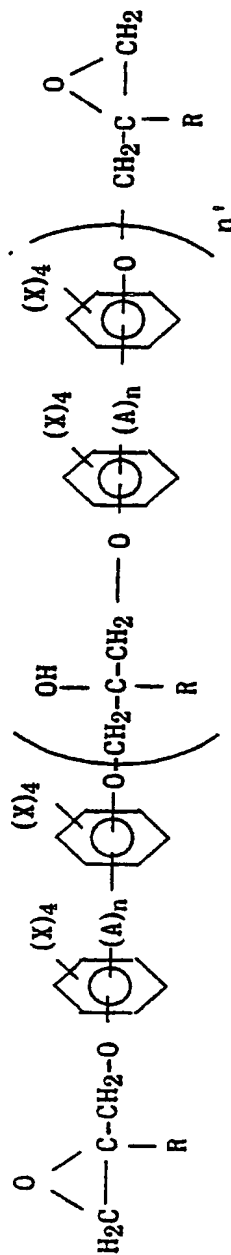
wherein each R¹ and R² are independently hydrogen or a hydrocarbyl or hydrocarbyloxy group having 1 to 12 carbon atoms or a -CH₂-O-R³ group wherein R³ is a hydrocarbyl group having from 1 to 12 carbon atoms; and each m and m' independently has a value from 1 to 25;

(b) component (A-1-b) is an epoxy resin or mixture of epoxy resins represented by the following formulas VII, VIII or IX or combinations thereof;

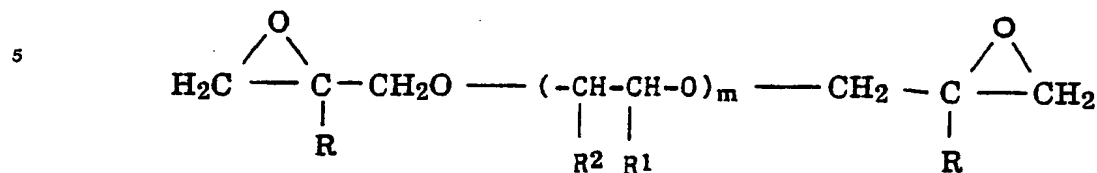
Formula VII



Formula VIII



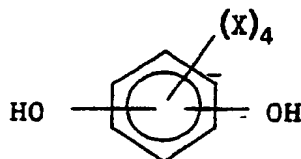
Formula IX



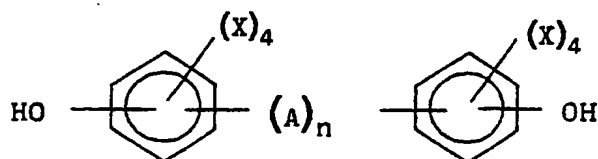
wherein A, R, R¹, R², X, m and n are as defined above and n' has an average value from zero to 5;

(c) component (A-2) is a compound or a mixture of compounds represented by the following formulas V and VI

Formula V



Formula VI



wherein A, X and n are as defined above; and

(d) component (B) is a volatile monoamine.

4. An advanced epoxy resin of Claim 3 wherein

(a) component (A-1-a) is a diglycidyl ether of the reaction product of bisphenol A with ethylene oxide, propylene oxide, butylene oxide, phenyl glycidyl ether, butyl glycidyl ether or a combination thereof;

(b) component (A-1-b) is a diglycidyl ether of bisphenol A, bisphenol F or a combination thereof; and

(c) component (B) is bisphenol A, bisphenol F or a combination thereof.

5. A modified advanced epoxy resin of Claim 1 or 2 which has additionally been reacted with a monocarboxylic acid.

6. A curable composition which comprises an advanced epoxy resin of Claim 1 or 2 and a curing quantity of a suitable curing agent for said advanced epoxy resin.

7. A curable composition which comprises an advanced epoxy resin of Claim 5 and a curing quantity of a suitable curing agent for said advanced epoxy resin.

8. A cured product resulting from curing the curable composition of Claim 5.



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 324 405 A3**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **89100260.2**

(51) Int. Cl.⁵: **C08G 59/06, C08G 59/14,
C08G 59/50**

(22) Date of filing: **09.01.89**

(30) Priority: **13.01.88 US 143771**

(43) Date of publication of application:
19.07.89 Bulletin 89/29

(84) Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE

(88) Date of deferred publication of the search report:
06.03.91 Bulletin 91/10

(71) Applicant: **THE DOW CHEMICAL COMPANY**
2030 Dow Center Abbott Road P.O. Box 1967
Midland Michigan 48640-1967(US)

(72) Inventor: **Massingill, John L., Jr.**
410 Forest Drive
Lake Jackson Texas 77566(US)
Inventor: **Pabon, Raul A., Jr.**
106 Mesquite
Lake Jackson Texas 77566(US)

(74) Representative: **Sternagel, Hans-Günther, Dr.**
et al
Patentanwälte Dr. Michael Hann Dr. H.-G.
Sternagel Sander Aue 30
W-5060 Bergisch Gladbach 2(DE)

(54) **Modified advanced epoxy resins.**

(57) Modified advanced epoxy resins are prepared by reacting (A) an advanced epoxy resin prepared by reacting (1) an epoxy resin having at least one aromatic ring, an average of more than one, but not more than about 2 vicinal epoxy groups per molecule and which contains at least one oxyalkylene or substituted oxyalkylene group per molecule; with (2) a dihydric phenol; with (B) a monoamine. Curable compositions comprising the modified advanced epoxy resin and cured products resulting from curing the curable compositions are also disclosed.

EP 0 324 405 A3



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 10 0260

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	US-A-4 507 461 (W.R. BOWDITCH et al.) * Claims * - - - -	1	C 08 G 59/06 C 08 G 59/14 C 08 G 59/50
A	US-A-4 339 369 (D.D. HICKS et al.) * Claims * - - - -	1	
A	US-A-4 608 405 (W.J. DeGOOYER) * Claims * - - - -	1	
P,X	EP-A-0 253 405 (DOW) * Claims; page 4, lines 17-36 * - - - -	1-8	
P,X	EP-A-0 253 404 (DOW) * Claims * - - - -	1-8	
E	EP-A-0 315 164 (KANSAI) * Claims * - - - - -	1-8	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 G
Place of search		Date of completion of search	Examiner
The Hague		29 November 90	DERAEDT G.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone		E : earlier patent document, but published on, or after the filing date	
Y : particularly relevant if combined with another document of the same category		D : document cited in the application	
A : technological background		L : document cited for other reasons	
O : non-written disclosure			
P : intermediate document		& : member of the same patent family, corresponding document	
T : theory or principle underlying the invention			